# PATENT SPECIFICATION

NO DRAWINGS

**876,226**

*Date of Application and filing Complete Specification: June 9, 1958.*
*No. 18386/58.*

*Application made in United States of America on July 23, 1957.*

*Complete Specification Published: Aug. 30, 1961.*

**Index at acceptance:—Classes 2(6), P4A, P4C(2: 3: 5: 6A: 8B: 9: 12A: 12B: 13A: 13B: 13C: 14A: 18: 20B: 20C: 20D1: 20D2: 20D3), P4D(1A: 2: 3A: 3B1: 3B3), P4K(4: 8: 9: 11), P7A, P7C(5: 8B: 9: 12A: 12B: 13A: 13B: 13C: 14A: 18: 20B: 20C: 20D1: 20D2: 20D3), P7D1A, P8A, P8C(2: 3: 5: 6A: 8B: 9: 12A: 12B: 13A: 13B: 13C: 14A: 18: 20C: 20D1: 20D2: 20D3), P8D(1A: 1B: 2A), P8(K4: T2D), P9A, P9C(2: 3: 5: 6A: 8B: 9: 12A: 12B: 13A: 13B: 13C: 14A: 18: 20C: 20D1: 20D2: 20D3), P9(D1B1: K4), P11A, P11C(2: 3: 5: 6A: 8B: 9: 12A: 12B: 13A: 13B: 13C: 14A: 18: 20B: 20C: 20D1: 20D2: 20D3), P11D(2X: 4: 7), P11K4; 96, B(2A: 3A), B14(C: D: F: H: X); and 140, E1(A: H).**

**International Classification:—C08f. D21h.**

COMPLETE SPECIFICATION

## Coating Compositions for Fibrous Materials

We, NOPCO CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of New Jersey, United States of America, of First and Essex Streets, Harrison, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coating compositions for fibrous materials such as paper, paperboard and textiles.

Many procedures have been carried out hitherto with varying degrees of effectiveness for the purpose of coating fibrous materials. The following characteristics are desired in order to obtain a useful coated product. The coated product in many instances must be flexible. The coating must be free from cracking. It must be free from sticking or blocking. The term "blocking" and expressions derived from it denote the undesirable property of adhesion between sheets of similar material when stacked under pressure, particularly at elevated temperature. In many applications a water repellant product is desired. If the coated product is to be used in connection with the packaging of foods and confections in which considerable shortening as well as moisture is present, the product must be grease resistant as well as water resistant. Concerning textiles, it is desired to have a coating which imparts a firm hand to the fabric without inducing boardiness. The expression "firm hand" means that the fabric feels firm to the touch. Also, in some uses, a coating which will gloss up upon calendering is required.

Polyvinyl acetate has been considered as a possibility for satisfying the aforementioned requirements, especially because of its low cost and very good adhesion to a base such as paper. However, polyvinyl acetate has a relatively low blocking temperature, thereby rendering a base coated with it of dubious value, particularly in summer months when temperatures are at their maximum. Also, polyvinyl acetate is not a good water resistant material. This resin when used alone on textiles tends to make the coated textile boardy, and if plasticizers are added to compensate for this, increased blocking occurs.

According to the present invention a coating composition suitable for application to a flexible, fibrous base comprises a blend of a plasticized polyvinyl acetate resin emulsion and a wax emulsion of a solid, non-tacky wax, the wax emulsion including a mildly acid-stable emulsifier, and there are present in the composition from 3 to 12 parts by weight of resin solids for each parts by weight of wax solids. The expression "solid, non-tacky wax" is used herein in a broad sense as including all substances which at room temperature are solid and non-tacky and which possess the physical characteristics normally associated with true waxes.

In this way the aforementioned desiderata have been unexpectedly achieved with polyvinyl acetate. In the case of a paper base coated with the blend, a coating characterized by excellent block resistant, greaseproof, waterproof, and flexing properties is obtained. Textiles so treated have a firm hand without boardiness and increased gloss upon subsequent calendering.

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It is recognized that resin emulsions including polyvinyl acetate emulsions are known and that wax emulsions are known; however, the blend of these two emulsions as specified above is novel. Moreover, the excellent results obtaining from the application of this novel blend to a fibrous base were most unexpected and could not have been predicted from the knowledge of the properties of resin emulsions and wax emulsions. The results obtained are believed to be due to the combined effect of all of the constituents contributing to and enhancing the effectiveness of each other in a synergistic manner.

The resin emulsion comprises an emulsion of either a homopolymer or copolymer of polyvinyl acetate. Generally the molecular weights of these polymers will be in the range of from about 100,000 to about 500,000.

When the homopolymer is used, i.e., polyvinyl acetate, then external plasticizers such as the following are added: dibutyl phthalate, hexylene glycol, dioctyl phthalate, di-2-ethylhexyl phthalate, dibutyl itaconate, diethyl phthalate, ethyl glycolate, methyl phthalate ethyl glycolate, and butyl phthalate butyl glycolate. These plasticizers may be present in an amount from about 2 to about 15% by weight of the homopolymer. If the composition is to be used for coating materials associated with foods, then an edible plasticizer would be required.

When it is desired to use copolymers of polyvinyl acetate in the resin emulsion several types may be used. One type of copolymer is an internally plasticized copolymer of vinyl acetate and a plasticizing inducing monomer copolymerizable therewith, the said monomer being present in an amount of up to 20% by weight of the copolymer. These copolymers are the preferred polymers used in the resin emulsion because they enhance flexibility as well as the antiblocking properties of the coated product to the greatest degree. Examples of comonomers which are useful in forming internally plasticized polymers of polyvinyl acetate are: dibutyl maleate, dibutyl fumarate, dioctyl fumarate, 2-ethylhexyl acrylate and vinyl stearate. One suitable copolymer emulsion contains about 52% by weight of a polyvinyl acetate copolymer comprising about 42% polyvinyl acetate and about 10% dibutyl maleate.

Cross-linked polymers of polyvinyl acetate may also be used since such polymers will result in higher blocking temperatures. Examples are vinyl acetate copolymerized with up to about 1.0% by weight of the final polymer of one of the following cross-linking inducing monomers: triallyl cyanurate, divinyl diethoxy silane, and diallyl phthalate. If these copolymers are used to form the resin emulsion, then an external plasticizer should be present in an amount of from about 2 to about 15% by weight of the homopolymer. Any of the plasticizers previously indicated as useful for plasticizing the homopolymer may be used for this purpose. The homopolymer or copolymer of polyvinyl acetate preferably comprises from about 40 to about 55% of the total weight of the resin emulsion.

There may also be present a protective colloid, in an amount of from ½ to 5.0% by weight of the resin emulsion. Since the resin emulsions are at a pH of from about 2 to 7, the protective colloid must be a mildly acid stable one in order to prevent it from precipitating out. Examples of useful colloids are polyvinyl alcohol, methylcellulose, sodium carboxymethylcellulose, hydroxyethylcellulose, polyacrylic acid, polymethacrylic acid and their alkali metal salts, e.g. sodium polyacrylate, and natural gums such as gelatin, lecithin, gum ghatti, gum tragacanth, gum arabic, and gum karaya. The presence of such a colloid in combination with the other ingredients will contribute to improved body, stability, blocking temperature and water resistance of the final composition.

The pH of the resin dispersion may be adjusted to a value of pH 4 to 5 by the addition of sodium citrate to the solution.

In order to ensure stability of the resin emulsion, it is preferred to have an emulsifier present in a small amount, e.g., from ½ to 5% by weight of said emulsion, such as the condensation product of 65% ethylene oxide and 35% octyl phenol, sulphated lauryl alcohol, sulphated isobutyl oleate, or the sodium salt of sulphonated dioctylsuccinate. Since the pH of the emulsion is from about 2 to 7, the emulsifier must be an acid stable one. The emulsifier must be one that is compatible with the resin in the resin dispersion as well as constituents of the wax dispersion.

The preparation of the aforementioned polymer or the final emulsion containing the polymer and protective colloid does not form a part of this invention. Various procedures for preparing the polymers and emulsion are known to those skilled in the art, all of which are satisfactory for producing the desired resin emulsion. For instance, all of the ingredients may be admixed and lastly, the monomers added dropwise to the mixture and polymerized in situ. The nature and amount of catalyst as well as the amount of heat are well known variables. Alternatively, batch polymerization may be used. In this instance all of the ingredients may be admixed together and the monomers then polymerized.

The second emulsion employed in the present invention contains wax, preferably in an amount of from 25 to about 50% by weight of the total wax emulsion, and an emulsifier. The wax must be a solid, non-tacky material rather than a liquid so that it will not penetrate the base upon which the blend is applied. All waxes, including the solid, non-tacky waxes are grease resistant in varying

degrees, but the wax should be so selected that it will strongly resist the solvent action of the particular grease with which it may come into contact. Examples of suitable waxes are natural waxes such as spermaceti, carnauba, curicuri, candelilla, Japan and the cane waxes derived from sugar cane. Mineral waxes may be used such as montan, ceresin, and lignite paraffin wax. Petroleum waxes such as the various paraffin and micro-crystalline waxes are also useful. Synthetic waxes which may be used include Scale wax, Santowax, (manufactured by Monsanto), hydrogenated vegetable fats including castor wax and hydrogenated cottonseed, soybean and corn oil. Also various polyethylenes are useful, as well as admixtures of polyethylenes with other waxes.

There may also be present in the wax emulsion a protective colloid in an amount from about ½ to 5.0% by weight of the emulsion. The colloid must be mildly acid and stable in order to prevent its precipitation when the wax emulsion is blended with the mildly acid resin emulsion. Examples are methylcellulose, sodium carboxymethylcellulose, hydroxyethylcellulose, polyvinyl alcohol and natural gums such as gum ghatti, gum tragacanth, gum arabic and gum karaya.

It has been found that the presence of an emulsifier is necessary to stabilize the wax emulsion. It must be mildly acid stable to prevent precipitation when the wax emulsion is blended with the slightly acid resin emulsion. The emulsifier may be present in an amount from about ½ to 1% by weight of the wax emulsion. Examples are fatty acid partial esters of hexitol anhydrides, e.g., the monolaurate, monooleate, and monostearate esters of hexitol anhydrides known as "Spans" (Manufactured by Atlas Powder Co.) ("Span" is a Registered Trade Mark), polyoxyethylene derivatives of the above, e.g. polyoxyethylene sorbitan monolaurate, known as "Tweens" (Atlas Powder Co.) ("Tween" is a Registered Trade Mark), sulphated isobutyl oleate, the sodium salt of sulphonated dioctyl succinate, the condensation product of 65% ethylene oxide and 35% octyl phenol, water-soluble salts of lignosulphonic acids, e.g., sodium lignosulphonate, the sodium salt of 2 mols of naphthalene sulphonic acid condensed with 1 mole of formaldehyde and sulphated fatty alcohols such as sulphated lauryl alcohol. These emulsifiers must be compatible with the wax in the wax emulsion as well as compatible with the ingredients in the resin emulsion.

The specific procedures for preparing these wax emulsions do not form a part of the present invention. Any method known to the art for emulsifying these materials may be used. In general, it is found desirable to mix together all of the solid ingredients at temperatures high enough to form a molten mass. Then the molten mass is admixed with water and emulsified in any conventional manner such as with a homogenizer or a colloid mill.

The two aforementioned emulsions, viz., the wax emulsion and the resin emulsion are combined to form a blend. This may be accomplished by simple stirring. The final blend must have present from 3 to 12 parts by weight of resin solids for each part by weight of wax solids. Preferably, there are from 3 to 6 parts by weight of resin solids present in the blend for each part by weight of wax solids. The amount of total solids per quantity of water present in the blend is not critical, but is merely a question of convenience, so long as the blend is stable. The total amount of water is, of course, influenced by the water present in each of the two emulsions before they are blended together. In fact, the concentration of the total solids may be varied depending upon the use of the blend, e.g., by dilution with water.

The blend may contain small quantities of pigment if desired. For instance, titanium dioxide and calcium carbonate may be used as opacifiers, particularly if the blend is to be applied to paper.

The following specific examples are given by way of illustration as to how the invention may be performed.

EXAMPLE I

(A) The resin emulsion was prepared in the following manner. All weight per cents are based upon total weight of the emulsion. The following ingredients were mixed together:

| | | Weight Per Cent |
|---|---|---|
| Vinyl acetate | — | 42.00 |
| Dibutyl maleate | — | 10.00 |
| Polyvinyl alcohol (Elvanol 51—05, Du Pont) | — | 2.00 |
| Polyvinyl alcohol (Elvanol 52—22, Du Pont) | — | 0.59 |
| Potassium persulphate | — | 0.15 |
| Condensation product of 65% ethylene oxide and 35% octylphenol | — | 0.20 |
| Water | — | 45.06 |

The resulting mixture was heated at a temperature of 190°F. for 45 minutes to bring about copolymerization of the vinyl-acetate and dibutyl maleate. At the conclusion of the polymerization, the pH of the reaction mixture was 2.75. This was adjusted to a pH of 4 to 5 by addition of sodium citrate. The reaction product, which was a copolymer of polyvinyl acetate in emulsion form was cooled and screened. The emulsion contained approximately 55% solids and had a viscosity of 1200 centipoises as determined by a Brookfield viscosimeter model LVF, spindle No. 3 at a speed of 60 r.p.m.

(B) The wax emulsion contained the following materials. All weight per cents are based upon the total weight of the emulsion.

| | | Weight Per Cent |
|---|---|---|
| Paraffin wax (M.P. 135° F.) | — | 14.00 |
| Castor wax (hydrogenated castor oil) | — | 14.00 |
| Cetyl alcohol | — | 0.90 |
| Gum ghatti (5% solution) | — | 20.00 |
| Marasperse N (sodium lignosulphonate, Marathon Corp.) | — | 0.50 |
| Water | — | 50.60 |

The wax emulsion was prepared by first melting the waxes together and heating to 110° to 125°C. Then the resulting wax melt was added with rapid agitation to the water which was previously heated to 95 to 98°C. The water also contained the emulsifying agents and protective colloid. The mix was then homogenized in a Manto-Gaulin Homogenizer at 3,000 pounds per square inch while the temperature was maintained at 95 to 98°C. The resulting wax emulsion contained 30% by weight of solids. The cetyl alcohol was used to improve the stability of the emulsion and to add lubricity to the wax.

(C) 69 parts by weight of the polyvinyl acetate emulsion of part A and 31 parts by weight of the wax emulsion of part B were mixed together by simple stirring in order to form the desired blend. The total solids content of the blend was 44% and the blend contained 4.1 parts by weight of resin solids for each part by weight of wax solids.

The following wax emulsions were prepared in a manner similar to the wax emulsion of Example IB. All figures represent per cent by weight of the total emulsion.

| Ingredients | Example No. II | III | IV | V |
|---|---|---|---|---|
| Paraffin wax (M.P. 135° F.) | 23.00 | | | 12.70 |
| Castor wax (hydrogenated castor oil) | | 28.90 | | 25.30 |
| AC Polyethylene Wax No. 617* | 15.35 | | | |
| Scale Wax | | | 37.50 | |
| Cetyl Alcohol | | | | 1.25 |
| Gum Ghatti Aqueous Sol'n. (5%) | 20.00 | 20.00 | 57.00 | 26.80 |
| Sodium lignosulphonate | 0.50 | 0.50 | | 0.75 |
| Water | 41.15 | 50.60 | 5.50 | 33.20 |
| % Solids (approximate) | 40.00 | 30.00 | 40.00 | 40.00 |

* This is produced by Semet-Solvay Petrochemical Div. of Allied Chemical and Dye Corp. and has an average molecular weight of 1500 and a melting point range of 88—90° C.

The wax emulsions of Examples II to V were blended by simple mixing with the resin emulsion of Example IA. The resulting blends are indicated below. All figures are per cent by weight of the total blend.

Wax Emulsion of Example

| | Example No. VI | VII | VIII | IX |
|---|---|---|---|---|
| II | 23.3 | | | |
| III | | 31.0 | | |
| IV | | | 23.3 | |
| V | | | | 23.3 |
| Resin Emulsion of Example IA | 69.0 | 69.0 | 69.0 | 69.0 |
| Water * | 7.7 | — | 7.7 | 7.7 |
| Total Solids | 44.0 | 44.0 | 44.0 | 44.0 |
| Ratio of resin/wax | 4.1/1 | 4.1/1 | 4.1/1 | 4.1/1 |

* This additional water was added in order to adjust the total solids content to 44%.

The coating compositions described herein may be applied to a variety of materials. Both woven and non-woven flexible, fibrous bases may be treated. It is of course understood that the term "fibrous" includes both continuous and spun filaments. For example, the following may be treated with these compositions: woven and non-woven natural and synthetic materials such as paper, paperboard, textiles such as wool, cotton, linen, viscose and acetate rayon. Nylon, glass, Dacron, Orlon, Dynel and Masslinn. "Dacron", "Orlon", "Dynel" and "Masslinn" are Registered Trade Marks. Also Cellophane (Registered Trade Mark) may be advantageously coated with the compositions.

Various coating procedures may be used such as spraying, padding or immersing, transfer rolls, knife coating, air knife coating, gravure coating or rod coating. However, the specific mode of coating does not form a part of the invention and may be any procedure known in the art that is convenient from a standpoint of handling these compositions. When paper is coated with the compositions, it is desirable that from $1\frac{1}{2}$ to 4 pounds of emulsion solids per 1000 square feet of paper be retained upon the paper. In the case of paperboard, the quantity of emulsion is selected so that about 3 pounds of emulsion solids per 1000 square feet of paperboard are retained thereon.

The blends of Examples IC and VI to IX were applied as coatings to samples of Hamilton bond paper. Wire wrapped rods (No. 40) manufactured by R and D. Specialties Co., Webster, New York, United States of America, were employed for this purpose. In this manner approximately three pounds of solids per 1000 square feet of paper were deposited on the paper. The coated paper samples were dried in an oven at 210°F. for 10 minutes to remove all the moisture.

To demonstrate the improved blocking resistance of the coated paper, the following procedure was carried out. The aforementioned samples were placed face to face and face to back and heated in an oven for 10 minutes at 80°C. under a one pound weight of one square inch cross section which covered a portion of the coated paper. A similar group of coated paper samples was heated face to back for 10 minutes at 110°C. under a one pound weight of one square inch cross section. The weights were subsequently removed, the samples cooled, and $\frac{3}{8}$ inch strips through the centre were cut out. The ends of the strips were clamped in a tensile tester made from a 2Kg. Ohaus balance and the force required to split the seal or to tear the paper was determined. The results are tabulated below.

| Paper Coated with Blend of Example | Heated face to face for 10 minutes | | Heated face to back for 10 minutes | |
|---|---|---|---|---|
| | 110° C. | 80° C. | 110° C. | 80° C. |
| IC | — | 50 gm | No tack | 30 gm |
| VI | — | 30 gm | 50 gm | 10 gm |
| VII | 50 gm | 10 gm | 70 gm | 10 gm |
| VIII | — | — | 40 gm | 20 gm |
| IX | — | 10 gm | 120 gm | 10 gm |
| Blank (resin emulsion only) | Tore paper | Tore paper | Tore paper | Tore paper |

WHAT WE CLAIM IS:—

1. A coating composition, suitable for application to a flexible, fibrous base, comprising a blend of a a plasticized polyvinyl acetate resin emulsion and an emulsion of a solid, non-tacky wax, the wax emulsion including a mildly acid stable emulsifier, and in which there are present from 3 to 12 parts by weight of resin solids for each part by weight of wax solids.

2. A coating composition as claimed in Claim 1 in which there are present from 3 to 6 parts by weight of resin solids for each part by weight of wax solids.

3. A coating composition as claimed in Claim 1 or Claim 2 in which the resin emulsion includes a mildly acid stable emulsifier.

4. A coating composition as claimed in Claim 3 in which the resin emulsion comprises from 40 to 55% by weight of plasticized polyvinyl acetate, from $\frac{1}{2}$ to 5% by weight of a mildly acid stable protective colloid and from $\frac{1}{2}$ to 5% by weight of mildly acid stable emulsifier.

5. A coating composition as claimed in Claim 4 in which the said protective colloid is polyvinyl alcohol.

6. A coating composition as claimed in any of the preceding claims in which the polyvinyl acetate is a homopolymer of vinyl acetate.

7. A coating composition as claimed in Claim 6 in which the plasticized polyvinyl acetate contains from 2 to 15% by weight of a plasticizer.

8. A coating composition as claimed in any of Claims 1 to 5 in which the polyvinyl acetate is a copolymer of vinyl acetate and another monomer.

9. A coating composition as claimed in Claim 8 in which the polyvinyl acetate copolymer is an internally plasticized copolymer obtained from vinyl acetate and a plasticizing inducing monomer copolymerizable therewith, the said

monomer being present in an amount up to 20% by weight of the copolymer.

10. A coating composition as claimed in Claim 9 in which the said monomer is dibutyl maleate.

11. A coating composition as claimed in Claim 9 in which there is present in the resin emulsion about 52% by weight of a polyvinyl acetate copolymer comprising about 42% polyvinyl acetate and about 10% dibutyl maleate.

12. A coating composition as claimed in Claim 8 in which the polyvinyl acetate copolymer is a cross-linked copolymer obtained from vinyl acetate and a cross-linking inducing monomer copolymerizable therewith, the said monomer being present in an amount up to 1.0% by weight of the copolymer.

13. A coating composition as claimed in any of the preceding claims in which the wax emulsion contains from 25% to 50% by weight of wax, from ½% to 5% by weight of a mildly acid stable protective colloid, and from ½% to 1% by weight of mildly acid stable emulsifier.

14. A coating composition as claimed in Claim 13 in which there are present in the wax emulsion, based on the weight of this emulsion, 14% paraffin wax and 14% hydrogenated castor oil.

15. A coating composition as claimed in Claim 13 in which there is scale wax present in the wax emulsion.

16. A coating composition as claimed in any of Claims 13 to 15 in which the protective colloid in the wax emulsion is gum ghatti.

17. A coating composition as claimed in any of the preceding claims in which the emulsifier of the wax emulsion is sodium lignosulphonate.

18. A coating composition as claimed in any of Claims 13 to 17 in which the wax comprises a polyethylene.

19. A coating composition substantially as described in any of the foregoing examples I(C) and VI—IX.

20. An article comprising a flexible, fibrous base coated with a composition as claimed in any of the preceding claims, which article is characterized by being greaseproof, blockfree, water repellent, and free from cracking upon flexing.

KILBURN & STRODE,
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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

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